

AD-A242 617



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GRANT or CONTRACT N00014-77-C-1234

R&T Code 413 h 012

Technical Report No. 6



HREELS and UPS Studies of  $\text{PH}_3$  and  $\text{PD}_3$  on Si(110)

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Prepared for Publication

in

Materials Letters

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## Abstract

The interaction of  $\text{PH}_3$  with  $\text{Si}(110)$  has been studied at temperatures between 120 and 880 K by UPS and HREELS. The results of HREELS measurements suggest that  $\text{PH}_3$  molecularly adsorbs on the silicon surface at 120 K with three distinct loss peaks at 60, 130 and 296 meV, corresponding to  $\nu(\text{Si-P})$ ,  $\delta(\text{PH}_3)$  and  $\nu(\text{PH}_3)$ , respectively. Heating of the surface to 300 K resulted in the dissociation of  $\text{PH}_3$ , producing  $\text{SiH}$ ,  $\text{PH}$  and  $\text{PH}_2$  species, with loss peaks near 263, ~270 and 288 meV, respectively. Further heating to 570 - 760 K caused a total loss of the 288 meV peak and the sharpening of the 263 and 270 meV peaks. At the highest surface temperature studied, 880 K, new loss peaks near 56 and 130 meV appeared. The combination of the UPS and HREELS data suggests that these loss peaks were due to the  $\text{P}_4$  molecule adsorbed on  $\text{Si}(110)$ . The HREELS study of  $\text{PD}_3$  was carried out to confirm the EELS assignments of  $\text{PH}_x$ . However, the heating of the adsorbed  $\text{PD}_3$  resulted in the desorption, rather than the decomposition of  $\text{PD}_3$ . This finding reveals the importance of the tunneling effect which appears to dominate the chemistry of  $\text{PH}_3$  on  $\text{Si}(110)$ .

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## 1. Introduction

Various phosphorus compounds have been employed for semiconductor doping and chemical vapor deposition (CVD) of thin films such as InP. Phosphine ( $\text{PH}_3$ ), one of the smallest stable P-compounds, has been used most commonly as a CVD source molecule [1-3]. Many studies have been made to elucidate the mechanisms of  $\text{PH}_3$  adsorption and decomposition on different metal surfaces, such as Rh(100) [4], Rh/ $\text{Al}_2\text{O}_3$  [5], Ag(111) [6], Pt(111) [7], Ni(100) [8] and polycrystalline Fe [9] under UHV conditions. Some experiments have also been conducted on silicon surfaces, including polycrystalline silicon [10], Si(111) [11,12], and Si(100) [13].

At low temperatures,  $\text{PH}_3$  may either molecularly adsorb or dissociatively adsorb on various surfaces, depending on the nature of surfaces. After thermal treatments, elementary phosphorus was observed. From the results of an XPS study, Yu et al. [13] suggested that  $\text{PH}_3$  binds nondissociatively to Si(100) at room temperature. However, the HREELS (high resolution electron energy loss spectroscopy) results of  $\text{PH}_3$  exposed on Si(111) [12] have indicated that mainly  $\text{PH}_2$  and H were present on the surface at temperatures as low as 80 K.

In order to understand the interaction of  $\text{PH}_3$  with the other low index silicon surface, we have investigated the interaction of  $\text{PH}_3$  with the Si(110) surface. The results of this study, using HREELS and

UPS (ultraviolet photoelectron spectroscopy), are reported here. Our results indicate that, initially,  $\text{PH}_3$  molecularly adsorbed on  $\text{Si}(110)$  at 120 K; as the surface temperature was increased, H, PH,  $\text{PH}_2$  and P species appeared on the  $\text{Si}(110)$  surface. When the surface was annealed at 880 K, the final product of  $\text{P}_4$  was identified by HREELS and UPS. A Similar HREELS of  $\text{PD}_3$  on  $\text{Si}(110)$  was also carried out in order to confirm the  $\text{PH}_3$  peak assignments.  $\text{PD}_3$  was, however, noted to be more stable than  $\text{PH}_3$  on the  $\text{Si}(110)$  surface. The heating of the surface resulted in the desorption rather than the decomposition of the adsorbed  $\text{PD}_3$  molecule. This interesting observation can be understood in terms of the well-known tunneling effect associated with the fragmentation of hydrides.

## 2. Experimental Procedures

The experiments were performed in a UHV system (Leybold Co.) with a base pressure of  $4 \times 10^{-11}$  torr, as described earlier [14]. Briefly, the HREEL spectrometer was operated with an electron beam which has a primary energy of  $E_p = 5$  eV and a resolution of  $\Delta E$  (FWHM) = 10 meV in the straight-through mode. UPS data was collect with a He II (40.8 eV) light source using a He-discharge lamp; the CMA detector was employed on the retard mode with a fixed pass energy of  $\Delta E/E = \text{constant}$ .

$\text{Si}(110)$  samples from Virginia Semiconductor Co. were cut into  $1.5 \times 1.0 \text{ cm}^2$  and mounted onto a sample holder with two Ta clips. After being rinsed with HF, the crystal was cleaned by successive

annealing to  $>1470$  K under UHV conditions until no carbon impurity can be detected by HREELS. Surface temperature was monitored by the combination of pyrometer, temperature-resistance calibration curve, and Pt-chromel thermocouple under different temperature ranges as reported elsewhere [14].

$\text{PH}_3$  (electronic grade, 2% in He, MG industries) was dosed directly into the chamber through a 3.2 mm SS tubing, about 4 cm from the crystal.  $\text{PD}_3$  was prepared in vacuo as follows. Dried  $\text{Ca}_3\text{P}_4$  (Aldrich Co.) was placed in a 100 ml 3-neck round-bottom flask, which was prebaked and connected in series to 3 traps maintained at 195, 195 and 77 K. After thorough pumping and degassing, 80%  $\text{D}_3\text{PO}_4$  in  $\text{D}_2\text{O}$  (Aldrich Co.) was slowly introduced into the sample flask through an evacuable dropping funnel. The first two dry ice traps (195 K) were used to remove vaporized  $\text{D}_2\text{O}$ ;  $\text{PD}_3$  was collected at the final liquid nitrogen trap (77 K). Final purification was made by distilling the 77 K condensate from 195 K to 77 K. FTIR analysis of the purified  $\text{PD}_3$  showed no detectable impurities and the D-atom enrichment was determined to be about 95%.

### 3. Results and Discussion

#### 3.1. HREELS of $\text{PH}_3$

Figure 1 shows the temperature dependence of the HREEL spectra of 1.8 L  $\text{PH}_3$  dosed on a Si(110) surface obtained under the specular mode. Immediately after dosing at 120 K, three loss peaks at 60, 130 and 296 meV were observed; these peaks may be

assigned to be  $\nu(\text{Si-P})$ ,  $\delta(\text{PH}_3)$ , and  $\nu(\text{PH}_3)$  vibrations, respectively. When the surface was warmed up to 300 K, the intensities of the peaks at 130 and 296 meV associated with the  $\text{PH}_3$  vibrations were greatly attenuated, while the shoulder around 87 meV and the two new peaks at 263 and 288 meV appeared. Earlier Lu et al. [5] showed, in their transmission IR absorption measurement for  $\text{PH}_3$  adsorbed on  $\text{Rh/Al}_2\text{O}_3$ , that  $\text{PH}_2$  and  $\text{PH}$  stretching vibration frequencies at about  $2270\text{ cm}^{-1}$  (281 meV) and  $2230\text{ cm}^{-1}$  (276 meV) could be identified. Accordingly, we assigned the 288 meV peak as the  $\text{PH}_2$  stretching vibration  $\nu(\text{PH}_2)$ , and the 263 meV peak as the  $\text{Si-H}$  vibration, perhaps with some contribution from the  $\text{PH}$  stretching vibration. Because of our instrument resolution ( $\approx 80\text{ cm}^{-1}$  or 10 meV), we cannot distinguish these two peaks clearly. The  $\nu(\text{PH}_2)$  peak at 288 meV is close to that assigned by Chen et al. [12], 280 meV for  $\text{PH}_2$  on  $\text{Si}(111)$ .

As the surface was further annealed at 670-760 K, the 288 meV peak almost disappeared entirely, while the 263 meV peak increased and, at the same time, shifted to 260 meV with a shoulder appearing at 270 meV, which may be assigned to the  $\text{PH}$  stretching vibration. In the meantime, the  $\text{Si-PH}_x$  peak at 87 meV decreased significantly and new peaks at 56 and 130 meV started to grow.

When the surface was annealed at 880 K, the latter two peaks became more distinct; these two peaks were tentatively assigned as  $\text{P}_4$  stretching vibrations. Because they compared quite favorably with the two gas-phase IR peaks of  $\text{P}_4$  at 58 and 133 meV reported by Gutowsky et al. [16].

It should be mentioned at this juncture that an earlier TPD experiment of  $\text{PH}_3$  on  $\text{Si}(111)\text{-(7}\times\text{7)}$  by Taylor et al. [11] suggested that  $\text{P}_2$ , instead of  $\text{P}_4$ , may be formed as a gas-phase product. The stretching frequencies of gaseous  $\text{P}_2$  or  $\text{P}_2\text{H}_4$  [17] are approximately 98 meV. Chen et al. [12] has shown that at temperatures higher than 850 K, only allotropes of phosphorus were left on the surface. Due to intensity problems, they cannot identify the products.

### 3.2. HREELS of $\text{PD}_3$

In order to confirm the peak assignments for  $\text{PH}_3$  on the  $\text{Si}(110)$  surface, we also measured the HREEL spectra of  $\text{PD}_3$  at different temperatures. Fig. 2 shows the HREELS of 1.1 L  $\text{PD}_3$  exposed on the  $\text{Si}(110)$  surface. After dosing  $\text{PD}_3$  at 120 K, two peaks clearly appeared at 92 and 218 meV, corresponding to the  $\text{PD}_3$  bending and  $\text{PD}_3$  stretching vibrations, respectively [7]. However, when the surface was annealed to 550 K, the  $\text{PD}_3$  EELS signals disappeared totally, suggesting that the  $\text{PD}_3$  molecule desorbed completely from the surface without a detectable decomposition product as was observed in the case of  $\text{PH}_3$ . This observation could only be accounted for by the assumption that the energy barrier for  $\text{PD}_3$  dissociation is higher than that for the desorption process. The fact that the dissociation of adsorbed  $\text{PH}_3$  does occur clearly suggests the importance of the tunnelling effect for the light phosphine molecule.

### 3.3. UPS of PH<sub>3</sub>

Figure 3 shows a series of UPS results of 1.8 L PH<sub>3</sub> on Si(110). All the spectra were plotted as the difference between the dosed and post-annealed surface and the clean surface. After dosing PH<sub>3</sub> at 120 K, the Si(110) valence states (Fig. 3f) at about 3 eV were reduced, and two major features located at 7.2 and 12.2 eV below the Fermi level were observed (fig. 3a). According to the UPS study of PH<sub>3</sub> on Ag(111) by Zhu and White [6], the energy separation between P(3s) 4a<sub>1</sub> and P-H 2e band was 5.0 eV. This agrees exactly with our results. However, the peak around 4.0 eV due to 5a<sub>1</sub> P lone pair was very weak; according to gas-phase He II UPS result of PH<sub>3</sub> by Bock [18], it should be about 3 eV lower in binding energy than that of the 2e peak.

When the surface was annealed at 270-590 K, a shoulder at 10.7 eV started to grow. Based on the result of Greenlief et al. [4] for PH<sub>3</sub> on Rh(100), P(3p) resulting from the partial dissociation of PH<sub>3</sub> should be contributed to the 10.7 eV peak. After the surface was annealed at 670 K, the 4a<sub>1</sub> band intensity began to decrease, and the 4.0 eV 5a<sub>1</sub> band structure became stronger. The valence state of Si(110) at 2.0 eV was reestablished again, while the transition due to PH<sub>x</sub> (x=1,2) grew weaker, which evidently resulted from the desorption of these species from the surface.

As the annealing temperature reached 870 K, a new peak appeared at 13.2 eV, and the 7.2 eV peak shifted to 6.9 eV. The energy difference between the two peaks was about the same as that



of the  $P_4$  gas-phase He II UPS result measured by Brundle et al. [19], who assigned those two peaks to be  $2e$  and  $5t_2$ , respectively.

#### **4. Conclusions**

The thermal stability of  $PH_3$  on Si(110) has been studied with HREELS and UPS.  $PH_3$  was found to molecularly adsorb on the Si(110) surface at 120 K. When the surface was warmed up to 300 K, the  $PH_3$  molecule started to dissociate into PH and  $PH_2$  as indicated by the disappearance of both the 130 meV  $\delta(PH_3)$  and 296 meV  $\nu(PH_3)$  frequencies and the growth of the peaks near 263 meV due to Si-H and P-H stretching frequencies, and the appearance of the 288 meV peak due to the  $PH_2$  stretching vibration. When the surface was further annealed at 670-760 K,  $PH_2$  and probably PH began to fragment further, as indicated by the decrease of the 288 meV peak and the shifting of the 263 meV peak to 260 meV, with a shoulder appearing at 270 meV. Finally at 880 K, the P species left on the Si(110) surface was concluded to be in the form of  $P_4$ . The result of a parallel experiment with  $PD_3$  showed that the  $PD_3$  adsorbed on Si(110) at 120 K undergoes desorption, rather dissociation, when the surface was heated up to 550 K. This result reveals clearly the importance of the tunnelling effect, which is responsible for the dissociation of the  $PH_3$  molecule as described above.

#### **Acknowledgment**

The authors gratefully acknowledge the support from the Office of Naval Research under contract No. N00014-89-J-1235.

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## Figure Captions

Fig. 1. HREELS spectra (from bottom to top) of clean Si(110), and  $\text{PH}_3$  exposed Si(110) surface at 120 K and after heating to various temperatures then cooling to 120 K. The initial exposure was 1.8 L.

Fig. 2. HREEL Spectra (from bottom to top) of clean Si(110), and  $\text{PD}_3$  exposed Si(110) surface at 120 K, and after heating to 550 K then cooling to 120 K. The initial exposure was 1.1 L.

Fig. 3. He (II) (40.8 eV) photoelectron Spectra of (f) clean Si(110), (a) - (e) 1.8 L  $\text{PH}_3$  exposed Si(110) at 120 K and after heating to various temperatures then cooling to 120 K.





